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(71) Applicant: UNITED TECHNOLOGIES CORPORATION [US/US]; United Technologies Building, Hartford, CT 06101 (US).

(72) Inventors: BORNSTEIN, Norman, S. ; 43 Richmond Lane, West Hartford, CT 06117 (US). CHIN, Stephen ; 9 Templeton Road, Wallingford, CT 06492 (US). DUHL, David, N. ; 31 Beacon Street, Newington, CT 06111 (US). PARILLE, Donald ; 6 Birch Hill Drive, South Windsor, CT 06074 (US). SHAH, Dilip, M. ; 95 Hampshire Drive, Glastonbury, CT 06033 (US).

(74) Agent: RASHID, James, M.; United Technologies Corporation, Patent Department, United Technologies Building, Hartford, CT 06101 (US).

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(54) Title: OXIDATION RESISTANT SINGLE CRYSTAL SUPERALLOY CASTINGS

(57) Abstract

Single crystal superalloy castings are described which have excellent oxidation resistance. The oxidation resistance is due to the presence of small but effective amounts of magnesium in the casting. Single crystal castings containing magnesium in the range of 5-200 parts per million, by weight, are described. Up to 100 % of the magnesium could be substituted by an equal atomic percent of calcium. The superalloy further consists essentially of, by weight percent, 1-12 chromium, 2-12 cobalt, 0-2.5 molybdenum, 3-10 tungsten, 0-8 rhenium, 2.5-13 tantalum, 0-2 titanium, 4.5-6.5 aluminum, 0-0.5 hafnium, 0-0.1 carbon, 0.0005-0.0200 magnesium, remainder nickel.

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# Description

## Oxidation Resistant Single Crystal Superalloy Castings

### Technical Field

This invention relates to single crystal castings having excellent oxidation resistance.

### Background Art

Materials used in the high temperature sections of modern gas turbine engines and other similar machines require an optimized combination of several properties, including mechanical properties as well as resistance to environmental degradation (oxidation and corrosion). Superalloys, based on nickel, cobalt, or iron, often possess these desired properties and have found widespread use in industry. The term "superalloys" is used to denote the class of refractory modified nickel, cobalt or iron based metal alloys specifically developed for high temperature service. Generally speaking, superalloys with the highest temperature capability have a single crystal microstructure. In other words, the casting is of a single grain, and has no internal grain boundaries. Single crystal castings are described in U.S. Patent No. 4,209,348 to Duhl et al., the contents of which are incorporated herein by reference. The Duhl et al. patent describes a single crystal superalloy casting having excellent mechanical properties and oxidation resistance.

Many superalloys owe their oxidation resistance to their ability to form a protective oxide film on the casting surface during use at elevated temperatures. The oxide film must be adherent in order for it to provide long term oxidation resistance. The most

protective films are generally considered to be aluminum oxide.

The element sulfur has been shown to detrimentally affect the ability of oxide films to adhere to the casting surface. Accordingly, a significant effort has been directed into removing sulfur from the casting or immobilizing sulfur in the casting. However, the prior art methods for addressing the sulfur problem have not been entirely successful. Accordingly, what is still needed in the superalloy industry is a method for dealing with sulfur and for making single crystal superalloy castings having the required levels of mechanical strength and oxidation resistance.

## Summary Of The Invention

This invention relates to the discovery that the single crystal nickel base superalloy castings containing small amounts of magnesium have excellent oxidation resistance. Single crystal castings according to this invention consist essentially of, by weight percent, 1-12 chromium, 2-12 cobalt, 0-2.5 molybdenum, 3-10 tungsten, 0-8 rhenium, 2.5-13 tantalum, 0-2 titanium, 4.5-6.5 aluminum, 0-0.5 hafnium, 0-0.1 carbon, 5-200 parts per million magnesium, balance nickel.

A specific composition within the most preferred range of compositions consists essentially of, by weight percent, 4.75-5.25 chromium, 9.5-10.5 cobalt, 5.6-6.2 tungsten, 8.4-9 tantalum, 5.5-5.8 aluminum, 1.7-2.1 molybdenum, 2.8-3.2 rhenium, 0.05-0.15 hafnium, 0-0.025 carbon, 0.001-0.007 magnesium, remainder nickel.

Single crystal castings in accordance with this invention have significantly improved oxidation resistance compared to prior art castings, and in

particular, compared to castings having a similar composition but lacking magnesium.

These and other features of the present invention will become apparent in light of the following description of the best mode for carrying out the invention, and the drawings.

## Brief Description Of The Drawings

Figure 1 is a schematic cross sectional view of a casting mold useful in making components in accordance with this invention.

Figure 2 is a graph which shows the oxidation resistance of single crystal castings in accordance with this invention, as compared to castings which are not in accordance with the invention.

## Best Mode For Carrying Out The Invention

Castings in accordance with the invention are made in the following manner. Master melts consisting essentially of, by weight percent, 1-12 chromium, 2-12 cobalt, 0-2.5 molybdenum, 3-10 tungsten, 0-8 rhenium, 2.5-13 tantalum, 0-2 titanium, 4.5-6.5 aluminum, 0-0.5 hafnium, 0-0.1 carbon, balance nickel are made. The master melt is then processed to produce single crystal castings using standard single crystal casting techniques, except for the fact that the casting molds are slightly modified from conventional practice. In particular, the casting molds are modified such that magnesium is intentionally introduced into the molten metal alloy while it solidifies in the mold. The molds are specifically modified such that 5-200 parts per million of magnesium are introduced into the casting as a result of a controlled reaction of the molten alloy

with a magnesium bearing ceramic material in the mold.

Figure 1 illustrates a casting shell mold 10 useful in carrying out the invention. The mold is made from a fugitive pattern (not shown), such as a wax pattern, that is alternately dipped in a ceramic slurry, stuccoed with ceramic particles and then dried in repeated fashion to build a shell mold about the pattern. The combination of the first layer of slurry and the first layer of stucco produces a face coat 15. The face coat 15 is backed by additional zircon and/or alumina containing layers of slurry and stucco 25, 30, respectively, in a manner typical of shell mold production. (Even though Figure 1 shows only two backup layers 25, 30, several more backup layers may be used, depending on the specific casting process utilized and the design of the desired casting.) The mold of this invention utilizes a magnesium bearing ceramic material, such as magnesia, in face coat 15. Between the backup layers 25, 30 and the face coat layer 15 is a barrier layer 20 comprised of alumina.

During the casting process, while molten metal is solidifying within the mold 10, the magnesium bearing material in the face coat 15 undergoes a reduction reaction to produce magnesium, which combines with the metal alloy in the mold. Tests have shown that such enrichment of the alloy with magnesium has a significant effect on the oxidation resistance of the resultant single crystal castings, as shown in Figure 2. The samples whose performance are shown in Figure 2 were tested in conventional cyclic oxidation tests at 1,150°C (2,100°F). One set of samples was cast into a mold intentionally containing magnesium bearing materials (in the form of a magnesia bearing face coat); the other set

of samples of like composition was cast into a mold which did not intentionally contain any magnesium bearing materials. The performance of the latter group of samples is considered typical of the prior art. It is apparent from Figure 2 that the single crystal castings of this invention have markedly superior oxidation resistance compared to the prior art specimens.

The following table sets forth the composition ranges of nickel base superalloy castings in accordance with this invention.

Composition Range (Weight Percent)

| Element | Broad | Preferred | Most Preferred |
|---|---|---|---|
| Chromium | 1-12 | 3.5-11.5 | 3.75-6.25 |
| Cobalt | 2-12 | 3.5-11.5 | 8.5-11.5 |
| Molybdenum | 0-2.5 | 0-2.5 | 0.7-2.5 |
| Tungsten | 3-10 | 3-7.2 | 4.6-7.2 |
| Rhenium | 0-8 | 0-4.2 | 1.8-4.2 |
| Tantalum | 2.5-13 | 7.4-13 | 7.4-10 |
| Titanium | 0-2 | 0-2 | 0 |
| Aluminum | 4.5-6.5 | 4.5-6.5 | 4.5-6.5 |
| Hafnium | 0-0.5 | 0-0.25 | 0.01-0.25 |
| Carbon | 0-0.1 | 0-0.05 | 0-0.025 |
| Magnesium | 0.0005-0.0200 | 0.0010-0.0100 | 0.0010-0.0070 |
| Nickel | Remainder | Remainder | Remainder |

See applicants' application IP 0004 - 007

A specific composition within the most preferred range of compositions is as follows: 4.75-5.25 chromium, 9.5-10.5 cobalt, 5.6-6.2 tungsten, 8.4-9.0 tantalum, 5.5-5.8 aluminum, 1.7-2.1 molybdenum, 2.8-3.2 rhenium, 0.05-0.15 hafnium, 0-0.025 carbon, 0.001-0.007 magnesium, remainder nickel. Single crystal castings having such composition have exhibited excellent

* claims

oxidation resistance in conditions which simulate the turbine section of advanced gas turbine engines.

The best improvements in oxidation resistance are achieved when the single crystal castings contain magnesium in the range of 0.0005-0.0200 weight percent; however, additions of calcium will also improve oxidation resistance. In particular, additions of calcium in an amount, by atomic percent, equivalent to 0.0005-0.0200 weight percent magnesium, are useful. Alternatively, up to 100% of the magnesium may be substituted for by an equal atomic percent of calcium.

While additions of magnesium to the casting is best accomplished through the use of a magnesium bearing mold system, as described above it may also be accomplished by intentional additions of magnesium to the master melt. In order to make single crystal castings in this manner, the casting process needs to be modified so as to prevent excessive loss of such magnesium in the single crystal casting process, to retain 0.0005-0.0200 percent magnesium in the finished single crystal casting.

Although this invention has been shown and described with respect to detailed embodiments thereof, it will be understood by those skilled in the art that various changes in form and detail thereof may be made without departing from the spirit and scope of the claimed invention.

## Claims

We claim:

1. A single crystal nickel base superalloy casting consisting essentially of, by weight percent, 1-12 chromium, 2-12 cobalt, 0-2.5 molybdenum, 3-10 tungsten, 0-8 rhenium, 2.5-13 tantalum, 0-2 titanium, 4.5-6.5 aluminum, 0-0.5 hafnium, 0-0.1 carbon, 0.0005-0.0200 magnesium, remainder nickel.

2. A single crystal superalloy casting, consisting essentially, by weight percent, 3.5-11.5 chromium, 3.5-11.5 cobalt, 0-2.5 molybdenum, 3-7.2 tungsten, 0-4.2 rhenium, 7.4-13 tantalum, 0-2 titanium, 4.5-6.5 aluminum, 0-0.25 hafnium, 0-0.05 carbon, 0.0010-0.0100 magnesium, remainder nickel.

3. A single crystal superalloy casting consisting essentially of, by weight percent, 3.75-6.25 chromium, 8.5-11.5 cobalt, 0.7-2.5 molybdenum, 4.6-7.2 tungsten, 1.8-4.2 rhenium, 7.4-10 tantalum, 4.5-6.5 aluminum, 0.01-0.25 hafnium, 0-0.025 carbon, 0.0025-0.0070 magnesium, remainder nickel.

4. A single crystal superalloy casting consisting essentially, by weight percent, 4.75-5.25 chromium, 9.5-10.5 cobalt, 5.6-6.2 tungsten, 8.4-9.0 tantalum, 5.5-5.8 aluminum, 1.7-2.1 molybdenum, 2.8-3.2 rhenium, 0.05-0.15 hafnium, 0-0.025 carbon, 0.001-0.007 magnesium, remainder nickel.

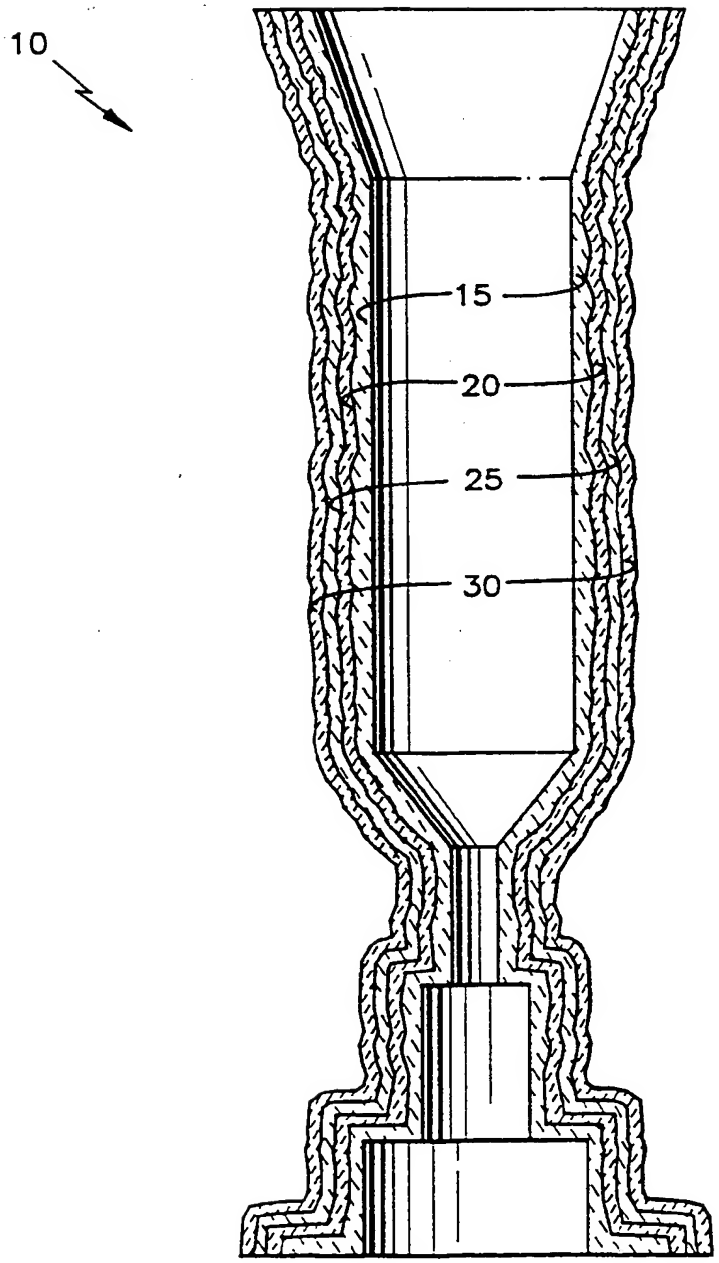
5. The casting of claim 1, wherein up to 100% of the magnesium is substituted for by an equal atomic percent of calcium.

6. The casting of claim 2, wherein up to 100% of the magnesium is substituted for by an equal atomic percent of calcium.

7. The casting of claim 3, wherein up to 100% of the magnesium is substituted for by an equal atomic percent of calcium.

8. The casting of claim 4, wherein up to 100% of the magnesium is substituted for by an equal atomic percent of calcium.

*fig. 1*



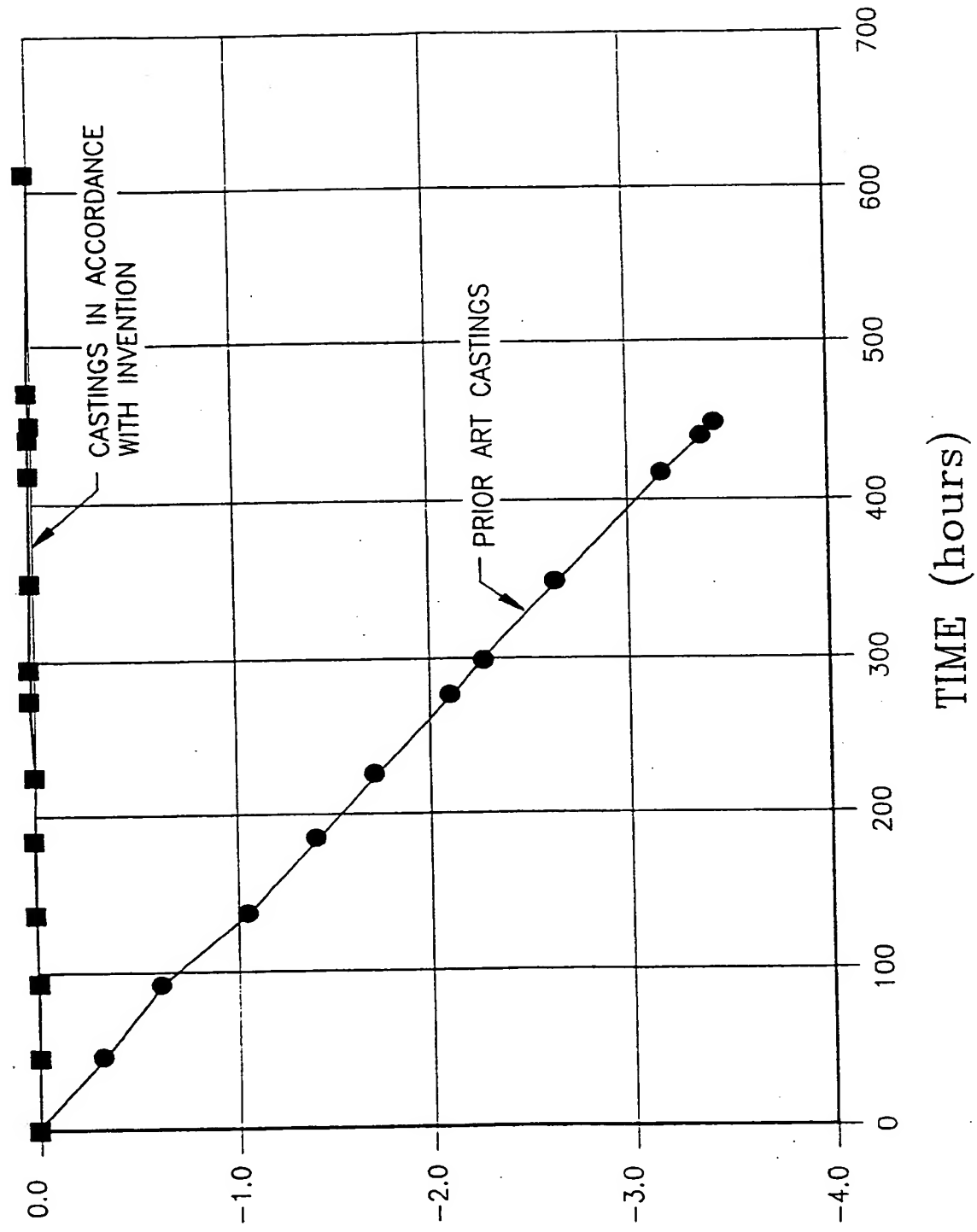



fig. 2

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 93/03803

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC$^5$: C 30 B 29/52,C 22 C 19/05

## II. FIELDS SEARCHED

Minimum Documentation Searched †

| Classification System | Classification Symbols |
|---|---|
| IPC$^5$ | C 30 B 29/00,C 30 B 21/00,C 30 B 11/00, C 22 C 19/00 |

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ‡

## III. DOCUMENTS CONSIDERED TO BE RELEVANT §

| Category * | Citation of Document, ‖ with indication, where appropriate, of the relevant passages ‡ | Relevant to Claim No. ‡ |
|---|---|---|
| X | EP, A1, 0 413 439 (CANNON-MUSKEGON CORPORATION) 20 February 1991 (20.02.91), claims. -- | 1-4 |
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| A | EP, A1, 0 052 911 (CANNON-MUSKEGON CORPORATION) 02 June 1982 (02.06.82), claims. ---- | 1 |

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## IV. CERTIFICATION

| Date of the Actual Completion of the International Search | Date of Mailing of this International Search Report |
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| 08 July 1993 | 18. 08. 93 |
| **International Searching Authority** | **Signature of Authorized Officer** |
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## ANHANG

zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

## ANNEX

to the International Search Report to the International Patent Application No.

## ANNEXE

au rapport de recherche international relatif à la demande de brevet international n°

PCT/US 93/03003 SAE 73739

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

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